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Infrared, electronic absorption spectra of 1-bromo-2,4- and 1-bromo-2,5-difluorobenzenes and electric dipole moments in the first excited electronic states of 1-bromo-2,4-, 1-bromo-2,5-, 1-bromo-3,4- and 1-bromo-3,5-difluorobenzenes

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The present note reports the analyses of the infrared and electronic absorption spectra of 1-bromo-2,4- and 1-bromo-2,5-difluorobenzenes in the vapour phase and also the estimation of the first excited state electric dipole moment of 1-bromo-2,4-, 1-bromo-2,5-, 1-bromo-3,4- and 1-bromo-3,5-difluorobenzenes using the solvetochromic shifts in different solvents.

The samples of 1-bromo-2,4-, 1-bromo-2,5, 1-bromo-3,4- and 1-bromo-3,5-difluorobenzenes used in this work were obtained from Aldrich Chemical Co, USA and were further purified before use. The experimental techniques used to record the vapour and solution phase electronic spectra and infrared (pure liquid phase) are the same as given in our earlier work (Shashidhar 1971).

1-Bromo-2,4- and 1-bromo-2,5-difluorobenzenes may be considered as belonging to the point group C_s if we consider the substituents to be coplanar with the benzene ring. The total number of 30 normal modes of vibration will have the distribution $21a' + 9a''$. The infrared absorption spectra have been analysed keeping in view the symmetry of the molecules and the analysed vibrational spectra of isomeric fluorobromobenzenes and similar substituted benzenes (Green 1970, Singh and Upadhya 1977, Verma and Shankar 1973, Narasimham *et al* 1956). The fundamentals so chosen are listed in Table 1, along with their assignments.

The electronic absorption spectra of the molecules studied show two $\pi^* \leftarrow \pi$ systems, one consisting of mostly well-defined bands around the wavelength 2800 Å and the other having some weak diffuse bands around 2200 Å. Even under the widely varied experimental conditions with the spectrograph used, it was not possible to improve the second system. This system was also recorded on a Hitachi U 3200 Spectrophotometer in vapour phase and in this record some bands were observed in the region 2000-2400 Å. The first system has been identified as corresponding to the forbidden electronic transition $^1B_{2u} \leftarrow {}^1A_{1g}$ of

Table 1. Fundamental vibrational frequencies (cm^{-1}) of 1-bromo-2,4- and 1-bromo-2,5-difluorobenzenes.

1-Br-2,4-DFB			1-Br-2,5-DFB			Assignment
IR	Electronic		IR	Electronic		
	G.S.	E.S.		G.S.	E.S.	
210 w	—	—	225 w	—	—	X-sensitive
235 w	—	—	240 w	—	—	X-sensitive
270 m	270 m	182 ms	265 m	—	161 m	X-sensitive
340 m	337 ms	230 ms	345 m	340 w	251 mw	X-sensitive
365 m	369 ms	250 s	385 m	—	—	X-sensitive
400 m	—	—	405 s	412 w	357 m	X-sensitive
465 s	462 m	428 ms	465 ms	—	413 m	X-sensitive
505 mw	—	—	525 m	—	—	C–C out-of-plane bend
550 ms	553 m	490 ms	575 ms	—	492 m	X-sensitive
600 s	605 m	556 ms	650 ms	—	540 mw	C–C in-plane bend
745 ms	—	—	765 vs	—	—	C–C out-of-plane bend
815 s	811 w	640 s	820 s	—	596 m	X-sensitive
855 vs	—	—	875 s	—	—	C–H out-of-plane bend
920 m	—	—	910 ms	—	—	C–H out-of-plane bend
960 vs	—	—	945 m	—	—	C–H out-of-plane bend

Table I. (Contd.)

1-Br-2,4-DFB			1-Br-2,5-DFB			Assignment
IR	Electronic		IR	Electronic		
	G.S.	E.S.		G.S.	E.S.	
1045 s	—	700 vs (732)	1040 s	—	806 ms (817)	X-sensitive
1115 s	—	947 m	1060 m	—	948 m	C–H in-plane bend
1150 vs	—	1051 s (1059)	1110 ms	—	1035 ms (1042)	C–H in-plane bend
1240 ms	—	1172 m	1200 vs	—	1187 m	X-sensitive
1270 s	—	1218 m	1225 m	—	—	X-sensitive
1295 ms	—	—	1260 vs	—	—	C–H in-plane bend
1310 m	—	1256 s	1300 m	—	1253 s	C–C stretch
1420 ms	—	—	1430	—	—	C–C stretch
1485 s	—	—	1480 s	—	—	C–C stretch
1585 ms	—	—	1550 m	—	—	C–C stretch
1605 s	—	—	1610 s	—	—	C–C stretch
3050 sh	—	—	3100 sh	—	—	C–H stretch
3080 w	—	—	3110 m	—	—	C–H stretch
3100 mw	—	—	3140 m	—	—	C–H stretch

Br—Bromo; DFB—Difluorobenzene; (.)—Values from $^1B_{1u} \leftarrow {}^1A_{1g}$ system.

benzene and the second system to $^1B_{1u} \leftarrow {}^1A_{1g}$ of benzene. Under the reduced symmetry C_s of the molecules, the above forbidden transitions become $^1A' \leftarrow {}^1A'$ and they are allowed.

The electronic absorption spectra of the first system of the molecules lie approximately in the region 2800 Å – 2500 Å. The effect of temperature on the band system has facilitated the choice of the band at 36555 and 36191 cm^{-1} as the 0, 0 band in 1-bromo-2,4- and 1-bromo-2,5-difluorobenzenes respectively. The identification of the fundamentals chosen has been mainly done on the basis of the intensities of the bands and the available literature on the analysis of $^1B_{2u} \leftarrow {}^1A_{1g}$ transition of other trisubstituted benzenes (Krishnamachari 1955, 1956, Sponer 1947, Tripathi and Pandey 1972, Singh and Pandey 1977). So chosen ground and excited state fundamentals are presented in Table 1. The strong bands on the longer wavelength side of 0, 0 band with spacing 18, 27 cm^{-1} in 1-bromo-2,4 and 31 cm^{-1} in 1-bromo-2,5-difluorobenzene have been identified as sequence intervals. The band data are with the authors.

The occurrance of the second system with little structure in the region 2400-2000 Å which has been correlated to the $^1B_{1u} \leftarrow {}^1A_{1g}$ system of benzene is of some interest in that this system though observed in several substituted benzenes usually do not exhibit structure. The existance of such additional band system has been reported in literature (Goel and Agarwal 1982, Amma *et al* 1969, Nair *et al* 1969). The bands observed towards the longer wavelength side at 47445

Table 2. Static dielectric constant (D) and refractive index (n) data for solvents and spectral data (ν_{max}) for solute molecules in solution.

Solvent	D	n	ν_{max} (in cm^{-1})			
			1-Br-2,4-DFB	1-Br-2,5-DFB	1-Br-3,4-DEB	1-Br-3,5-DFB
Cyclohexane	2.0240	1.4260	36300	35909	36208	37109
Carbon tetrachloride	2.2368	1.4595	36274	35857	—	37081
Chloroform	4.8100	1.4460	36353	—	36247	37081
iso-Propanol	20.3170	1.3770	·	36038	36313	37150
n-Propanol	21.2400	1 3837	36432	36025	36326	37136
Methanol	5.7000	1.3290	36512	36117	36379	37191
Ethenol	3.4710	1.3600	36472	36064	—	37164
Dichloromethane	9.0800	1.4240	36406	—	36287	—
Diethylether	4.2294	1.3506	36432	36051	36313	37164
1-Butanol	18.2700	1.3985	—	35999	—	37122
n-Heptane	1.9200	1.3770	· ·	—	36234	—

and 46561 cm^{-1} in 1-bromo-2,4- and 1-bromo-2,5-difluorobenzenes respectively have been identified as 0, 0 bands. The indentified excited state fundamentals are also listed in Table 1 and they are correlated to the fundamentals of 2600 Å system.

The electric dipole moment of 1-bromo-2,4-, 1-bromo-2,5-, 1-bromo-3,4- and 1-bromo-3,5-difluorobenzenes in their first excited electronic state has been

calculated using a method given by Ayachit et *al* (1986), from the solvent effect on their electronic spectra. The ν_{max} values observed for $^1A' \leftarrow {}^1A'$ transition which are given in Table 2 are used to calculate μ_e and θ, the angle of μ_e with

Table 3. Electric dipole moments and θ.

Molecule	Ground state electric dipole moment in Debye units μ_g	Excited state electric dipole moment in Debye units μ_e	θ in degrees
1-Br-2,4-DFB	1.53	3.26	45
1-Br-2,5-DFB	2.31	4.33	55
1-Br-3,4-DFB	1.45	2.74	41
1-Br-3,5-DFB	1.47	3.08	63

respective μ_g. The values of refractive index (n) and dielectric constant (D) of solvents used are taken from literature (Weast 1973-74) and are also given in

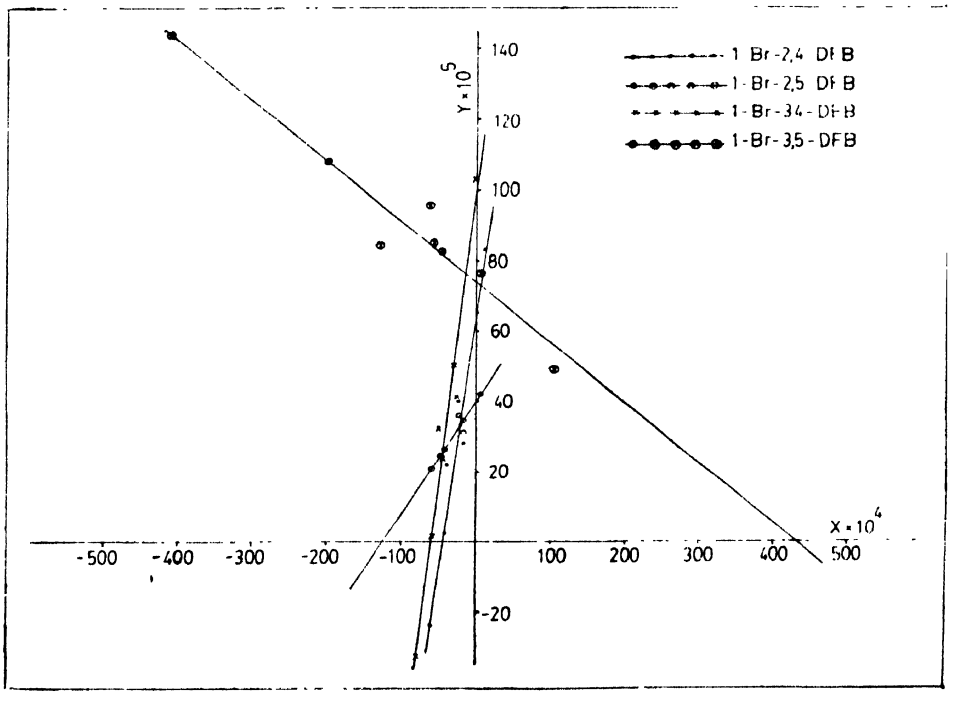

Figure 1. X vs Y plots for 1-bromo-2,4-, 1-bromo-2,5-, 1-bromo-3,4- and 1-bromo-3,5-difluorobenzenes.

Table 2. The ground state electric dipole moments of these molecules were determined as given in our earlier work (Aralakkanavar and Shashidhar 1989) and

are given in Table 3. The molecular radius has been calculated using the method of atomic increments (Edward 1956) and is found to be 3.002 Å for these molecules.

The relevant plots obtained for the observed system of the molecules are given in Figure 1. The values of μ_e and θ are given in Table 3 which shows that the dipole moments in the excited state of these molecules are higher than their ground state values indicating that the observed band system in the molecules studied is due to $\pi^* \leftarrow \pi$ transition, which is consistent with published observations (Shashidhar *et al* 1976, Ayachit *et al* 1988, Deshpande *et al* 1981, Tonannavar *et al* 1987, Jaffe and Orchin 1962) made on the basis of the solvent effect on the system.

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